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*Original Scientific Paper*

# Determination of Dissolved Monomethylmercury in Saline, Estuarine and Fresh Waters of Croatia

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Measurements of dissolved monomethylmercury (MeHg) (which included both the dissolved part and the part leached from the particles by addition of 2 M HCl) were carried out in natural waters of various origin and composition (fresh, estuarine saline and brackish water, saline coastal water and groundwater). Following a proper water sampling procedure, MeHg was leached by hydrochloric acid, preconcentrated on a sulphydryl cotton fibre (SCF), eluated with hydrochloric acid, decomposed, and detected as $Hg^0$ by a cold vapour atomic absorption spectrometry (CVAAS). The MeHg concentrations determined in the water samples of the Krka River Estuary, groundwaters (landfill »Jakuševec«, in the vicinity of Zagreb), and the Kaštela Bay were: $3.5 \times 10^{-14}$ to $7.5 \times 10^{-13}$ mol dm$^{-3}$, $2.0 \times 10^{-13}$ to $3.0 \times 10^{-12}$ mol dm$^{-3}$, and $1.0 \times 10^{-12}$ to $2.0 \times 10^{-11}$ mol dm$^{-3}$, respectively. The concentration of MeHg in the water column of the Krka River Estuary is inversely related to reactive mercury. The MeHg maximum is just above a fresh/saline water interface (FSI), whereas maximums of the reactive and total mercury are below and/or inside the FSI. Winds and other meteorological conditions exert significant influence upon the distribution of MeHg concentrations in the water column. The performance of the modified analytical procedure was improved, yielding a high recovery efficiency of MeHg (85–96%), reproducibility better than 15% (CV) and the limit of detection of $3.5 \times 10^{-14}$ mol dm$^{-3}$, *i.e.* 0.007 ng L$^{-1}$ (3 $\sigma$ of the blank) for water sample of 3 L.

*Key words:* speciation, mercury, dissolved monomethylmercury, estuarine waters, seawaters, groundwaters.

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## INTRODUCTION

Investigations of the biogeochemical processes of mercury in a natural aquatic environment as well as estimation of the present state of water pollution by mercury require reliable data. Therefore, it is very important to be able to distinguish between the background natural levels of various mercury species and the anthropogenic input.

The presence of different chemical species of mercury in an aquatic environment is significant from the ecological point of view because of their different toxicities. Monomethylmercury, MeHg, is one of the most toxic and dangerous forms of mercury. It is very efficiently concentrated through biological membranes and, at a certain level, its effects on mammals may be neurotoxic, teratogenic, embrio-toxic, and genetic.[1]

Even very low monomethylmercury concentrations may still have harmful effects upon the aquatic environment owing to a high enrichment factor, its biomagnifying behaviour, as well as very efficient accumulation.

Regardless of the concentrations in the aquatic environment, the MeHg, accumulates in living organisms through the trophic chain where, depending on the position of the biota in the foodweb, it may represent from 10 to 25% (in phytoplankton and shellfish) up to 99% (in fish) of total mercury.

Our preliminary investigations on the uptake of mercury species by transplanted mussels *Mytilus galloprovincialis* under estuarine conditions showed that the accumulation efficiency for methylmercury is about 50 times higher than that for total mercury. Only 1% of the total mercury content, and 20–50% of the methylmercury content in water filtered by the mussels is accumulated in shellfish tissues,[2] while the bioconcentration factor of MeHg (ambient water/edible part of mussels) is about $10^4$. This factor is much higher for fishes due to their high position in the trophic chain. For example, the bioconcentration factor for an annular git head (*Diplodus annularis*) (polluted part of the Kaštela Bay) is about $10^6$, and for a bluefin tuna (*Thunnus thynnus*), one of the main aquatic predator fishes, is as high as $10^8$.[3]

Such biomagnification processes often increase the MeHg levels in fish, frequently exceeding the WHO acceptable concentrations for the edible part of fishes, 0.5 mg $kg^{-1}$ fresh weight (FW).[4] In short, only a few kilograms of mercury released into the natural aquatic environment by such processes can endanger cubic kilometers of such media. Because of the MeHg bioconcentration from the sub-part per trillion levels in natural waters to the part-per-million levels in fish and other aquatic human food, reliable and accurate data on the MeHg content in an aquatic system, regardless of its very low natural levels, are of utmost importance.

## EXPERIMENTAL

### *Study Areas, Sampling and Sample Pretreatment*

The Krka River Estuary (Figure 1a) is located in the central part of the eastern Adriatic coast. It may be classified as a highly stratified estuary for the most part of the year.[1] This water system has been extensively investigated, particularly concerning mercury.[2,5–8] Hydrological and chemical features of the estuary are described elsewhere.[9]

The Kaštela Bay (Figure 1b) is situated on the eastern Adriatic coast in the vicinity of the city of Split. It is the largest bay in central Dalmatia and the most threatened one along the eastern Adriatic coast with regard to the release of mercury from a chlorine-alkali plant (the production of chlorine was discontinued in 1990).[10]

Groundwater sampling was performed in the vicinity of the city of Zagreb (landfill »Jakuševec«)[11] (Figure 1c).

Estuarine and seawater samples were collected from the water column at a particular depth with the diver facing the direction of the current, and opening and closing the sampling bottle with outstretched hands. This sampling method proved to be particularly efficient for sampling in stratified estuaries at intervals as small as 5 cm,

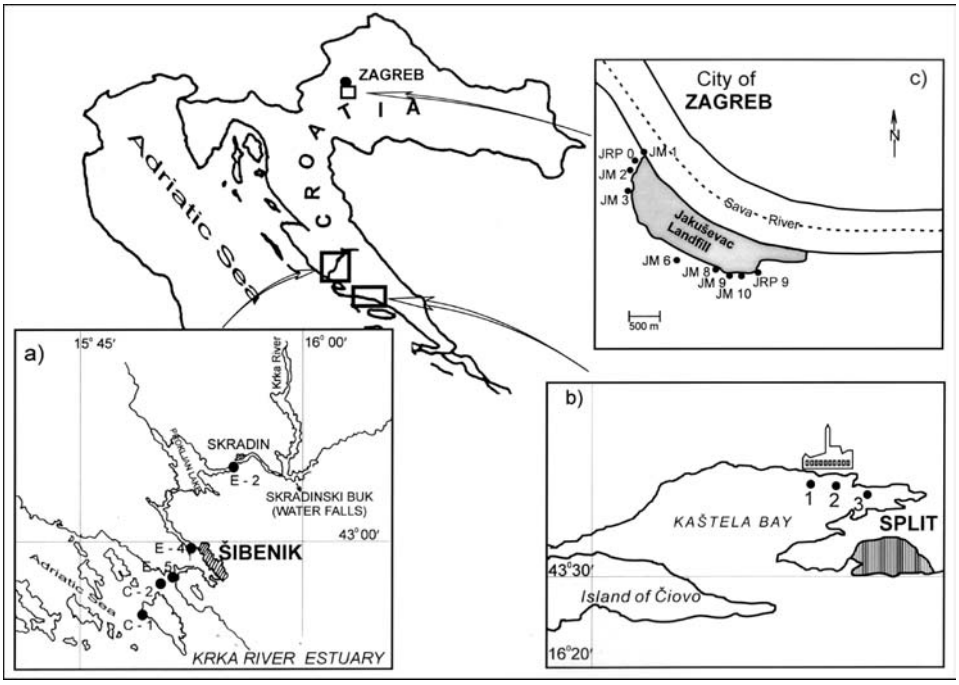


Figure 1. Map of the sampling areas.

with clear visibility of the boundary between the incoming river water and seawater (FSI, fresh/saline water interface).[1,6]

Groundwaters were sampled using PTFE tubing, immersing the pumps into the water at various depths.[11]

Pyrex-glass bottles, cleaned in advance with nitric and hydrochloric acid and rinsed with tapwater, were used as samplers and containers. All samples were acidified »on the spot« with 3.5 mL 2 M HCl per litre, and the bottles, wrapped in alufoil, were kept refrigerated at +5 °C until analysis. Determination of mercury species was performed within 24 hours of sampling (except for groundwater samples).

### *Reagents*

Doubly-deionized water was used for the preparation of reagents and solutions, as well as for rinsing some parts of the equipment. Since tap water in the Martinska Laboratory (Šibenik) contains low total mercury concentrations (0.1–0.4 ng $L^{-1}$), and no MeHg has been detected, it was used for cleaning and rinsing the sampling bottles.

All the reagents used in this work were of analytical or »suprapure« grade (Merck, Germany). Extra pure nitrogen (Linde, Germany) was used as purging gas and sample carrier during CVAAS (cold vapour atomic absorption spectrometry) procedure, as well as for controlling the flowrate of the sample during separation on the SCF column.

The working MeHg standard solutions (200 ng $mL^{-1}$, 20 ng $mL^{-1}$ and 10 ng $mL^{-1}$) were prepared from the concentrated MeHgCl stock solution (4 mg $L^{-1}$).

The SCF (sulphydryl cotton fibre) adsorbent was synthesized from thyoglicolic acid, acetic acid, acetic anhydride, sulphuric acid, water and cotton.[12] The formed SCF adsorbent (kept refrigerated in a dark glass bottle) could be utilized for up to 6 months with no changes.

### *Analytical Procedure*

The method applied for the MeHg determination in aqueous samples requires a sequence of several analytical steps (Figure 2).

The unfiltered water sample of 1 L (sample volume 1 to 5 L can be used) was acidified by adding 3.5 ml 2 M HCl (pH ≈ 3.0).

0.5 g of the SCF adsorbent was packed into a pyrex glass column (10 mm I.D. × 3 mm I.D. of a bottom outlet × 12.5 mm O.D. × 220 mm in length) connected to a 1 L pyrex glass bottle, which was refilled with the required volume of the sample up to 5 L.

Acidified and unfiltered water samples passed through the SCF adsorbent in the column at a flowrate of 15 mL $min^{-1}$, which was adjusted by nitrogen gas pressure.

The MeHg adsorbed on the SCF in the column was eluated with 10 ml 2 M HCl only. No ionic mercury was detected in the eluate. Ionic mercury was partly processed through the column with the samples during the preconcentration step, but a larger quantity (> 90%) remained adsorbed on the SCF adsorbent after the MeHg separation. The eluate was collected in a quartz tube wrapped in alufoil (as a protec-

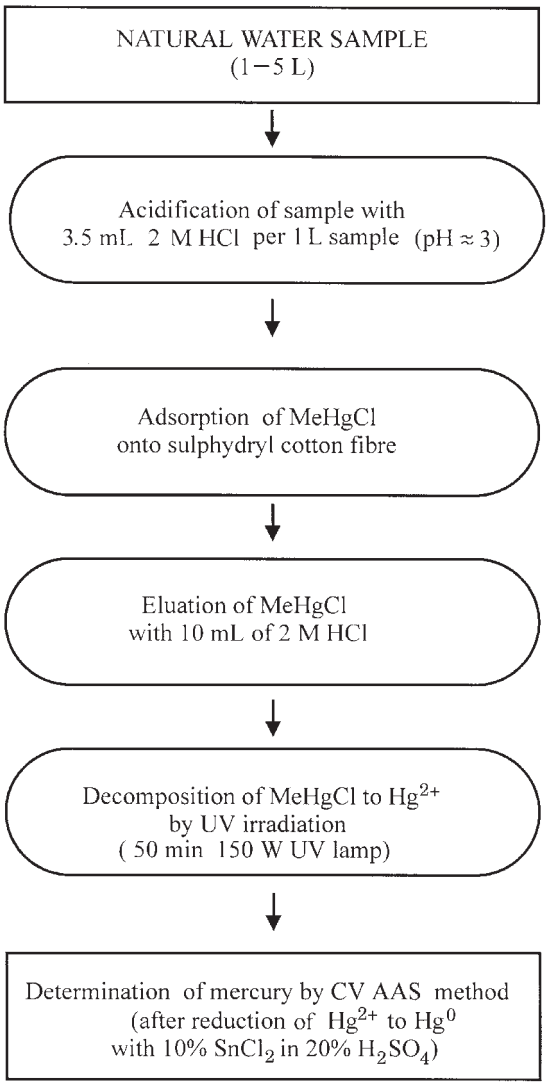


Figure 2. Schematic flow-chart of MeHg determination in natural waters.

tion against light decomposition of MeHg). The aliquot taken from 10 ml of eluate was measured prior to and after the decomposition of MeHg to $Hg^{2+}$ by the UV-irradiation during 50 min using a 150 W UV lamp, Hanau, Germany.

### *Detection System*

Cold vapour atomic absorption spectrometry was used for mercury measurements. This method requires conversion of all forms of mercury to $Hg^{2+}$ (acid, oxida-

tive digestion) and its reduction to $Hg^0$ by the $Sn^{2+}$ solution (10% $SnCl_2$ in 20% $H_2SO_4$), adsorption/desorption on Au-wire and detection of $Hg^0$ vapour by atomic absorption spectrometry. The detection limit of such a modified CVAAS system is 5 pg with the linearitiy range from 0.005 to 10 ng. The reproducibility is 2% for concentrations > 200 ng $g^{-1}$ or > 1 ng $L^{-1}$, and ≤ 10% for concentrations > 1 ng $g^{-1}$ or > 0.1 ng $L^{-1}$. The efficiency is > 80% for liquid matrices, and > 90% for solid matrices. Details of the procedure are described elsewhere.[5,13] The following instruments were used: an Atomic Absorption Spectrometer, Perkin-Elmer model 410 and/or an Elemental Mercury Detector (mercury MONITOR™ 3200 by Thermo Separation Products).

## RESULTS AND DISCUSSION

Determination of dissolved methylmercury in water was carried out in brackish and saline water samples along the Krka River Estuary (stations E2, E4 and E5) and coastal stations (C2 and C1) (Figure 1a). The results obtained for the samples collected in May and July of 1996 and 1997 are summarized in Table I. For determination of the vertical distribution of mercury species, the samples were collected twice in May of 1997 (Table II). The MeHg concentrations obtained ranged from 0.04 to 0.150 ng $L^{-1}$ as a part of the total (0.7–9%), and of the reactive mercury (0.8–13%). These results are in satisfactory agreement with the data published for other unpolluted aquatic environments, *e.g.* the sub-polar North Atlantic region.[14] Total and occasionally reactive mercury species were also measured in order to compare the ratios between different mercury species. Total mercury was measured in unfiltered and acidified water samples (pH ≈ 1) after the UV-irradiation during 24 hours with a 150 W UV lamp, while the reactive mercury was measured directly in unfiltered and unacidified water samples using a CVAAS method (see *Detection system*). Reactive mercury represents inorganic and labile mercury compounds that are reactive in a solution of stannous chloride in sulphuric acid.[5] The Krka River Estuary is a highly stratified water system and its water column is characterized by a pronounced, sharp interface (FSI) between freshwater and seawater. In the upper part of the water column above the FSI (salinity 0–20‰), only 10–50% of total mercury is reactive, while below the FSI (salinity 35–38‰), 80–100% of total mercury is reactive.

The distribution of mercury species at the FSI in the Krka River Estuary showed multiple peaks of reactive and total mercury. This was particularly evident in the upper part of the estuary near the Skradinski Buk waterfalls.[6] The preliminary results obtained for MeHg showed that its peak concentration was not observed in/or below the FSI (salinity 20–34‰), but at the upper edge of the FSI (salinity of 7 and 8‰). The reactive mercury content was the lowest at this level of the water column (Table II). This was also observed on many occasions during the Hg measurements. The results

TABLE I

Methylmercury (MeHg), reactive and total mercury concentrations / ng $L^{-1}$ at different stations and depths along the Krka River Estuary

| Station (Sample vol. / L) | Depth / m Salinity / ‰ | MeHg Reactive Hg Total Hg $c$[a] / ng $L^{-1}$ | Recovery efficiency of spiked MeHg / % |
|---|---|---|---|
| E4 (3) | 0.2 | 0.17 ± 0.08 ($n$ = 5)[b] | 95 |
| | 3–5 | 0.7 | |
| | | 1.7 ± 0.6 ($n$ = 5) | |
| | 3–5 | 0.11 ± 0.1 ($n$ = 5) | 92 |
| | 38 | 1.8 | |
| | | 2.00 ± 0.9 ($n$ = 5) | |
| E5 (3) | 0.2 | 0.05 ± 0.016 ($n$ = 3) | 93 |
| | 30 | – | |
| | | 1.4 ± 0.13 ($n$ = 3) | |
| C2 (3) | 0.1 | 0.02 ± 0.01 ($n$ = 4) | 85 |
| | 38 | 0.63 | |
| | | 0.70 ± 0.1 ($n$ = 4) | |
| C1 (3) | 0.1 | 0.017 ± 0.009 ($n$ = 4) | 88 |
| | 38 | 0.44 | |
| | | 0.60 ± 0.1 ($n$ = 4) | |
| E2 (3) | 0.2 | 0.034 ± 0.01 ($n$ = 2) | 95 |
| | 3 | 0.25 | |
| | | 1.50 ± 0.5 ($n$ = 2) | |
| | 6.0 | 0.143 ± 0.02 ($n$ = 2) | 88 |
| | 38 | 1.90 | |
| | | 2.30 ± 0.35 ($n$ = 2) | |

[a] mean ± SD;
[b] $n$, number of samples.

obtained show that the concentrations of dissolved monomethylmercury are inversely proportional to the reactive mercury.[15,16] These results may be explained by different kinetics between an increase of the reactive mercury concentrations and a delay of the corresponding methylation processes.

The influence of stormy winds on the concentrations of the reactive and total mercury in the water column of the Krka River Estuary is described elsewhere.[6] Similar effects of winds on the MeHg distribution in the water column (station E2) (Figure 1) were also observed after twenty days of an

TABLE II

Vertical distribution of methylmercury (MeHg), reactive and total mercury concentrations in the Krka River Estuary water column at station E2

| Depth / m | Salinity / ‰ | $c$ / ng $L^{-1}$ | | | $w$ / % | |
|---|---|---|---|---|---|---|
| | | MeHg | Reactive Hg | Total Hg | MeHg / React. Hg | MeHg / Total Hg |
| | | | A | | | |
| 0.2 | 2 | 0.04 | 0.90 | 2.0 | 4.4 | 2.0 |
| 2.2 | 8 | 0.09 | 0.70 | 2.5 | 12.8 | 3.6 |
| 2.5 | 36 (FSI) | 0.04 | 1.30 | 2.4 | 3.0 | 1.7 |
| 6.0 | 37 | 0.04 | 1.70 | 4.3 | 2.4 | 0.9 |
| | | | B | | | |
| 0.2 | 2 | 0.130 | 2.0 | 3.5 | 6.5 | 3.7 |
| 2.7 | 7 | 0.150 | 1.5 | 1.6 | 10.0 | 9.4 |
| 2.9 | 34 (FSI) | 0.090 | 2.5 | 3.4 | 3.6 | 2.6 |
| 3.0 | 37 | 0.090 | 10.5 | 12.5 | 0.9 | 0.7 |
| 3.5 | 38 | 0.070 | 9.1 | 10.2 | 0.8 | 0.7 |
| 6.0 | 38 | 0.060 | 6.3 | 6.3 | 0.9 | 0.9 |

A – 8$^{th}$ May 1997, B – 28$^{th}$ May 1997.
FSI – fresh / saline water interface.

intensive Bura (northern) wind (Table I), after two weeks of calm weather (Table IIA), and at the outset of a strong Bura wind (Table IIB). The influence of wind on the distribution of the MeHg concentrations (along the vertical water column) at the same station is obvious. The lowest concentrations of MeHg (0.007 ng $L^{-1}$) were found in the surface water at station C1 (Table I) after a strong Bura wind, whereas more than ten times higher levels of dissolved MeHg (0.110 ng $L^{-1}$) (Table V) were observed following a predominant southern (Jugo) wind.

The winds cause formation of two opposite currents in the Krka River Estuary which continue to flow in two different water layers. Vertical circulation in saline waters is directed from the bottom to the halocline (FSI), while in fresh waters, the circulation is oriented from the surface to the halocline.[17]

The opposite currents stir up waters, *i.e.*, winds influence the transfer and mixing of the contents from different parts of the water column (surface, FSI, bottom), thus affecting the salinity gradient and mercury species distribution. To understand the biogeochemical cycle of mercury species in such a complex aquatic environment, as well as the methylation process, the conditions of the water column should be defined.

Seawater samples from the Kaštela Bay were collected at three stations: in the vicinity of the outfall of a chlorine-alkali plant (production was discontinued in 1990) (no. 1); a station about 100 m to the east (no. 2); and 350 m offshore of the town of Kaštel Sučurac (no. 3). Some of the sediments of the Kaštela Bay, which are found to be heavily polluted by mercury, are limited to the proximity of the PVC factory, thus the concentrations of mercury species decrease going offshore or along the shore.[10,18]

Table III shows that the MeHg and total mercury concentrations in water decrease 30 and 35 times from station 1 to station 3 (a distance less than 500 m), respectively. In contrast to quantity, the percentage of MeHg (as a fraction of total mercury) increases in the same direction, from 0.35% (at station 1) to 3% (at station 3). One can conclude that the biogeochemical production of MeHg in this area is relatively slow. This may be due to the oxidation and demethylation by specific organisms or the availability of the mercuric ion as the main substrate for methylation. Recent investigations of volatilization of mercury from the Kaštela Bay waters, by detection of $Hg^0$ and of $(CH_3)_2Hg$ formed from the mercuric ion,[19] lead to the same explanations as those of the results published for other regions.[20]

The influence of winds on mercury concentrations in the waters of the Kaštela Bay was also observed. In January, the aquatorium was under a strong influence of the intensive Jugo wind, but in February the weather was calm and windless. As a result, the seasonal content of MeHg and total mercury in the water column at the same stations (Table III) differed significantly.

TABLE III

Methylmercury (MeHg) and total mercury concentrations / ng $L^{-1}$ in the Kaštela Bay water

| Date | Station | $c$ / ng $L^{-1}$ | | $w\left(\frac{\text{MeHg}}{\text{Total Hg}}\right) \Big/ \%$ | Recovery efficiency of spiked MeHg / % |
|---|---|---|---|---|---|
| | | MeHg | Total Hg | | |
| 27/01/97 | 1 | 3.60 | 451.00 | 0.8 | 89 |
| 13/02/97 | | 1.40 | 400.00 | 0.35 | |
| 27/01/97 | 2 | 1.20 | 168.00 | 0.7 | 85 |
| 05/02/97 | | 0.30 | 76.00 | 0.4 | |
| 13/02/97 | | 0.15 | 71.00 | 0.2 | |
| 27/01/97 | 3 | 0.16 | 13.60 | 1.2 | 81 |
| 05/02/97 | | 0.20 | 6.40 | 3.0 | |
| 13/02/97 | | 0.14 | 6.00 | 2.3 | |

In addition to the MeHg determinations in estuarine and coastal unpolluted and polluted waters of Croatia, the method described was successfully applied for the first time to (fresh) groundwaters. The sampling was carried out at 7 piezometers near the Sava River and the main landfill of the city of Zagreb.[11] The results summarized in Table IV are in good agreement with, otherwise scarce, published data for the Hg concentrations in groundwaters.[21]

Compared with other methods,[22–24] this one requires a larger volume of the water sample (1–5 L) for MeHg measurements. Nevertheless, the suitability of the method for determination of MeHg in estuarine waters, particularly highly stratified ones, with a very low content of total mercury and MeHg, such as the Krka River Estuary, has been experimentally demonstrated. Besides, several types of water, with different physical, chemical, and biological features that appear in the water column, affect different mercury speciations.[6,7] There is no need to adjust or change any step of the procedure (method) due to the alteration of water composition in the water column.

For each type of water in which MeHg was determined, the recovery efficiency was evaluated by addition of standard solutions of 20 and 2 ng of MeHg.

TABLE IV

Methylmercury (MeHg) and total mercury concentrations / ng $L^{-1}$ in some groundwater samples from the city of Zagreb

| Location of sampling | Date | $c$ / ng $L^{-1}$ | | $w\left(\frac{\text{MeHg}}{\text{Total Hg}}\right) / \%$ | Recovery efficiency of spiked MeHg / % |
|---|---|---|---|---|---|
| | | MeHg | Total Hg | | |
| JM 8 | | 0.11 | 0.90 | 12.2 | 90 |
| JM 9 | | 0.12 | 1.80 | 6.6 | |
| JM 10 | June 1995 | 0.24 | 3.70 | 6.5 | |
| JRP 9 | | 0.38 | 4.70 | 8.0 | 86 |
| JRP 0 | | 0.60 | 4.70 | 12.8 | 77 |
| JM 1 | | 0.09 | 1.1 | 8.2 | 90 |
| JM 2 | | 0.19 | 2.6 | 7.3 | |
| JM 3 | May 1997 | 0.04 | 0.6 | 6.6 | 95 |
| JM 6 | | 0.20 | 1.7 | 11.8 | |
| JM 9 | | 0.15 | 1.3 | 11.5 | 92 |

In all tables, the amount of spiked MeHg recovered from various types of water is denoted with concentrations.

The reproducibility was tested on three sets of samples collected from two different stations; brackish water samples (E2 station) and surface saline water samples (C1 station) (Table V). For each station/depth, the samples were collected at a same time under the same meteorological conditions. The precision of the method is between 6% and 15% (CV).

TABLE V

Reproducibility of measurements of methylmercury concentrations at two different stations in the Krka River Estuary. For each station and depth, the samples were taken at the same time (May 1997)

| Station | Depth / m | Salinity / ‰ | No. of sampling repetitions | Result of repetitive measurements: $c$(MeHg) / ng $L^{-1}$ | | Mean ± SD / ng $L^{-1}$ | Coefficient of variation / % |
|---|---|---|---|---|---|---|---|
| | | | 1. | 0.035 | 0.035 | | |
| E2 | 0.2 | 3 | 2. | 0.026 | 0.026 | 0.037 ± 0.002 | 5 |
| | | | 3. | 0.040 | 0.040 | | |
| | | | 1. | 0.11 | 0.10 | | |
| C1 | 0.2 | 38 | 2. | 0.08 | 0.08 | 0.091 ± 0.014 | 15 |
| | | | 3. | 0.10 | | | |

## CONCLUSIONS

The dissolved MeHg was successfully determined in natural water samples of different origin and composition using the method described. The detection limit of the method is $3.5 \times 10^{-14}$ mol $dm^{-3}$ (0.007 ng $L^{-1}$) for 3 L of water sample with reproducibility better than 15% (CV). The recovery efficiency of spiked MeHg mostly ranged from 85% to 96%. Relatively high volume of the sample required for measurements (mostly 3 L; even 5 L of pristine water presented no experimental difficulties) may be considered as a drawback, but the procedure is relatively simple, few chemicals are used, and there are no in-between analytical steps that might be a source of difficulty. The applied procedure enables MeHg measurements in unpolluted natural waters with an extremely low ($10^{-14}$ mol $dm^{-3}$) content of dissolved MeHg.

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## SAŽETAK

### Određivanje otopljene monometilžive u slanim, estuarijskim i slatkim vodama Hrvatske

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Otopljena monometilživa (MeHg) (sastavljena od otopljenog dijela i dijela koji se oslobađa nakon dodatka 2 M HCl) određivana je u prirodnim vodama različitog porijekla i sastava (slatkim, slanim i estuarijskim). Nakon uzorkovanja autonomnim ronjenjem i zakiseljavanja uzoraka s HCl, otopljena MeHg adsorbirana je na koloni s adsorbensom SCF (sulphydryl cotton fibre). Iz kolone je eluirana s pomoću 2 M HCl te je s ultraljubičastim svjetlom prevedena u ionsku živu. Otopinom $SnCl_2$ u $H_2SO_4$ reducirana je ionska živa u metalnu, te adsorpcijom/desorpcijom na zlatnoj žici određena atomskom absorpcijskom spektrometrijom (metoda hladnih para). Nađeni su koncentracijski rasponi otopljene MeHg u vodama estuarija rijeke Krke ($3{,}5 \times 10^{-14}$ do $7{,}5 \times 10^{-13}$ mol $dm^{-3}$), u podzemnim vodama Zagreba (u blizini odlagališta smeća Jakuševec) ($2{,}0 \times 10^{-13}$ do $3{,}0 \times 10^{-12}$ mol $dm^{-3}$), te u vodama Kaštelanskog zaljeva ($1{,}0 \times 10^{-12}$ do $2{,}0 \times 10^{-11}$ mol $dm^{-3}$). U vodenom stupcu estuarija rijeke Krke otopljena MeHg nalazi se u obrnutom koncentracijskom odnosu prema reaktivnoj živi. Njezin se koncentracijski maksimum nalazi odmah iznad međusloja (slatko-slana voda) za razliku od reaktivne i ukupne žive čiji je koncentracijski maksimum u samom međusloju ili neposredno ispod njega. Raspodjela otopljene MeHg u vodenom stupcu pod snažnim je utjecajem meteoroloških uvjeta, osobito vjetra. Modificirana i za različite tipove prirodnih voda prilagođena metoda ima visoku učinkovitost (85–95%), te reproducibilnost bolju od 15% (CV), uz osjetljivost određivanja od $3{,}5 \times 10^{-14}$ mol $dm^{-3}$ odnosno 0,007 ng $L^{-1}$ (tri standardne devijacije od slijepog pokusa) za volumen uzorka od 3 L.